

THERMAL CONDUCTIVITY OF SOLIDS

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Introduction to thermal conductivity

1.1 The significance of heat conduction

Human appreciation of the importance of the conduction of heat begins with the well-known fact that some things, a piece of metal for instance, feel cold to the touch while others, for example a piece of wood, feel warm. The reason for this is that metal conducts heat away from the body faster than wood. All-year-round human occupation of the temperate and colder parts of the Earth's surface has always depended on the ability to control the loss of heat from the body. Amongst the things that feel warm because of their low thermal conductivity are the furs, skins, and woven cloth used by mankind for millenia for protection against external cold. Similar considerations govern the choice of building materials, particularly in more recent times under the impact of technology employing the results of scientific analysis of heat transfer. The reverse problem arises in a spacecraft, where it is necessary to keep the astronauts cool during re-entry into the Earth's atmosphere.

These examples all call for materials of low conductivity, but other situations require a high rate of heat transfer. For example the need to protect certain semiconductor devices from damage due to overheating has led to the semiconductor being mounted on a diamond heat sink, diamond having a higher thermal conductivity around room temperature than any metal. This is an extreme case, but there are many others where efficiency requires the transfer of heat with a minimum temperature difference.

Thus we sometimes need a high, sometimes a low thermal conductivity. Often this will be associated with a requirement of good mechanical strength or high electrical conductivity, and so on. This reveals that the study of thermal conductivity often requires a context of materials science, in the widest sense.

It will be clear that the existence of a body of data on thermal conductivity and related properties will never suffice to meet the problems posed by technology. What is also needed is theoretical understanding which will enable us to predict the thermal conductivity of new materials, and to guide us in our attempts to find materials to cope with new requirements. In turn the testing of theories will challenge the experimenters by requiring new standards of accuracy in measurement.

The interaction of theory and experiment has influenced the layout of this book. It begins with some preliminary questions of definition and so forth and then goes on to describe the methods by which accurate data can be obtained. This is followed by an outline of the theory and of the ways in which it may be applied to experimental results. Finally, the behaviour of everyday practical materials is reviewed and considered.

1.2 Thermal conductivity: Fourier's law

The first clear statement of the proportionality of heat flow and temperature gradient was made in 1822 by Fourier in his *Theorie Analytique de la Chaleur*. It should be realised, however, that this kind of linear law does not apply to other forms of heat transfer such as convection or radiation where, although the heat flow is some function of the temperatures of the two regions involved, this function will generally be by no means simple. In fact in the case of solids a lack of proportionality between apparent heat flow and temperature gradient would often be regarded as evidence that some nonconductive mechanism was at work. This might be due to a deficiency in the experimental arrangement or, very rarely, in the case of some materials transparent in the infrared there might be a genuine component of heat transfer by radiation.

The linear proportionality of heat flow and temperature gradient may be supposed to be observed in a situation where there is a flat slab of material of thickness Δx whose faces are isothermal surfaces but at temperatures differing by an amount ΔT . We suppose that there is some means of measuring the heat flow into and out of these surfaces. If the slab is effectively thermally insulated at the edges and there are no internal sources of heat, such as electric currents or radioactivity, then in a steady state the rate of heat flow Φ into one face equals that out of the other. We then find that for a given slab

$$\Phi \propto \Delta T,$$

and if we take varying thicknesses of slab then

$$\Phi \propto \frac{\Delta T}{\Delta x}.$$

Furthermore, if we now vary the area A of the slab,

$$\Phi \propto A \frac{\Delta T}{\Delta x};$$

this relation may then be used to define the thermal conductivity λ thus

$$\Phi = -\lambda A \frac{\Delta T}{\Delta x}.$$

From this line of argument it is possible to generalise to a vector heat current density

$$U = -\lambda \text{grad } T. \quad (1.1),$$

The minus sign arises from the fact that heat always flows from the hotter to the colder region. Equation (1.1) will be the form of Fourier's law generally used in this book.

There are a number of qualifications which must be made with reference to this line of argument:

(i) Since the thermal conductivity is a function of the temperature, if one works back from equation (1.1) to the original expression in terms of ΔT , this will clearly break down if ΔT becomes large enough to encompass significant changes in λ .

(ii) Some materials are anisotropic with respect to heat conduction and it will be seen that this will mean that the heat flux vector U will not necessarily be parallel to $\text{grad } T$. This requires the generalisation of (1.1) to a form which can be expressed either by

$$U = -\lambda \text{grad } T, \quad (1.2a)$$

where λ is written as a dyadic, or by

$$U_i = - \sum_j \lambda_{ij} \frac{\partial T}{\partial x_j}; \quad (1.2b)$$

we have introduced here a tensor λ_{ij} having nine components, of which no more than six may be different, because where $i \neq j$, $\lambda_{ij} = \lambda_{ji}$. Equation (1.2b) will sometimes be found without the summation being explicitly written in, but then it is understood that repeated suffixes are summed over. Fortunately, for polycrystalline materials and cubic crystals the simple equation (1.1) will suffice.

(iii) Although the vectors U and $\text{grad } T$ are defined as though at a point in the solid, there will clearly be difficulties of a conceptual kind if this is regarded too literally, since neither U nor $\text{grad } T$ can have any meaning for a single atom in a solid. Theoretical discussion always assumes that these quantities are in fact defined with respect to regions which, although small, contain enough atoms for the fluctuations in U and $\text{grad } T$ to be negligible.

(iv) There may be problems relating to measurements on rather small but otherwise completely homogeneous samples where, if the cross-sectional area is decreased, the heat current decreases more than proportionally. This 'size effect', as it is called, really means there is no properly defined thermal conductivity at all, but in practice the concept of a size-dependent 'effective' thermal conductivity is used.

Another question concerns whether there are any subsidiary conditions necessary for the meaningful measurement of thermal conductivity. There appears at present to be only one, and this is that no electric current must be flowing in the material under examination. The reason for this is that, if there is a current, then the Peltier heating where the current enters and leaves the material under investigation may be inadvertently added to the heat carried by conduction. Furthermore, there may be additional interference due to the Thomson effect. Electric currents would not normally be deliberately passed through a specimen during a thermal

conductivity experiment without these effects being allowed for, but under some circumstances there might be currents passing due to the Seebeck effect which would pass unnoticed. The most desirable way of proceeding is to ensure open circuit conditions during the measurement of thermal conductivity, unless the passage of a current is essential to the method being employed. As a definition of thermal conductivity we must add to equation (1.1) the condition

$$j = 0, \quad (1.3)$$

where j is the electric current density.

1.3 Conservation of energy and the definition of thermal diffusivity

The linear law relating heat flow and temperature gradient gives only a partial description of the thermal processes involved in solids. In particular it is adequate only for steady state phenomena with no internal sources of heat. To go further requires the use of the principle of conservation of energy, otherwise known as the first law of thermodynamics.

Let us consider a small volume inside the conducting medium (the meaning of 'small' is that discussed in the previous section). Then, if there is no work being done on this volume, the change in its internal energy will be given by the heat transfers across its boundaries. Thus, if ΔE_0 is the internal energy at time $t = 0$, and ΔE_t that at time t , then

$$\Delta E = \Delta E_t - \Delta E_0 = \Delta Q,$$

where ΔQ is the heat entering the small volume. This can be expressed in terms of the time derivative of the internal energy and the heat current integrated over the surface S :

$$\frac{d(\Delta E)}{dt} = - \int U \cdot n dS,$$

where n is an outward directed normal to the surface. The term on the left-hand side can be replaced by a volume integral over the internal energy density E , whilst the right-hand side can be replaced by a volume integral, using Gauss's theorem. Then

$$\int \frac{\partial E}{\partial t} d^3x = - \int \text{div } U d^3x,$$

or, since the integration volume is arbitrary,

$$\frac{\partial E}{\partial t} = - \text{div } U. \quad (1.4)$$

The changes in internal energy can be expressed in terms of the specific heat c multiplied by the density $\hat{\rho}$:

$$\frac{\partial E}{\partial t} = c\hat{\rho} \frac{\partial T}{\partial t} = - \text{div } U,$$

or, combining with Fourier's law (equation 1.1),

$$c\hat{\rho} \frac{\partial T}{\partial t} = \text{div}(\lambda \text{ grad } T). \quad (1.5)$$

This equation requires further discussion and elaboration. To begin with, is the specific heat referred to that at constant pressure, c_p , or constant volume, c_v ? As the argument was presented above there is no doubt that c_v is appropriate, since work of any kind was excluded, which means no changes in volume. However, this is not the usual experimental situation, since it requires rigid constraints around the conductor to prevent the normal change of volume by thermal expansion. If we use the condition of constant pressure, then the place of the internal energy E must be taken by the enthalpy H , in which case the correct specific heat to employ is c_p . In actual fact a body containing temperature differences normally also contains internal stresses and for that reason c_p is not quite appropriate either. But with a simple one-dimensional temperature gradient c_p is likely to be more nearly correct.

The form of equation (1.5) allows for the possibility of the thermal conductivity varying with position, either owing to the temperature gradient or to actual inhomogeneity of the conductor. However, in most work this effect is neglected and (1.5) is written

$$c\hat{\rho} \frac{\partial T}{\partial t} = \lambda \nabla^2 T,$$

or

$$\frac{\partial T}{\partial t} = a \nabla^2 T, \quad (1.6)$$

where $a = \lambda/c\hat{\rho}$ is called the thermal diffusivity. Equation (1.6) is essential in all discussions of time-varying thermal phenomena in homogeneous media; there are appropriate modifications to allow for anisotropic conductors. In the case of steady temperatures equation (1.6) reduces to Laplace's equation, $\nabla^2 T = 0$.

In deriving equation (1.4) it was assumed that there was no work being done, and it was subsequently shown that the possibility of the performance of work to change the volume affected the proper definition of the specific heat in (1.5). However, there are other examples involving work which can be better regarded as heat generation within the conductor, although this is not a very well-defined concept from the thermodynamic point of view. As an example, if there is an electric current density j and an electrical conductivity σ (assumed scalar), then an external electromotive force is doing a quantity of work j^2/σ in unit volume, which is normally expressed as a heat generation of j^2/σ per unit volume. In this case equation (1.4) becomes

$$\frac{\partial E}{\partial t} + \text{div } U = \frac{j^2}{\sigma}. \quad (1.7)$$

For any other process involving work done within the conductor there will be a corresponding term added to equation (1.4) in the same way.

It has been pointed out that an equation such as (1.6) has certain rather implausible consequences. If we consider for example a flat slab and apply at a given instant a supply of heat to one face, then according to (1.6) there is an instantaneous effect at the far face. This of course cannot occur in practice, since no signal can be propagated through the slab at infinite velocity. One way of avoiding this is to modify (1.6) as follows:

$$\nabla^2 T = \frac{1}{a} \frac{\partial T}{\partial t} + \frac{1}{u^2} \frac{\partial^2 T}{\partial t^2}, \quad (1.8)$$

where u is a quantity having the dimensions of velocity. If u is made equal to the velocity of sound, then the paradox of instantaneous propagation is avoided, but the effect of this term is less than that of the first for times greater than a/u^2 . For a good conductor these times are about 10^{-11} s and they are even shorter for poor conductors. For all practical purposes therefore equation (1.6) is quite satisfactory.

1.4 The physical mechanisms of the conduction of heat in solids

In section 1.2 it was shown how it is possible to discuss heat conduction in solids in terms of a single coefficient, the thermal conductivity, and in section 1.3 equations were derived whose solutions describe the temperature distribution in a solid. Subsequently these equations will be applied in analysing the experimental methods used to determine the conductivity. In this section a survey is given of the physical processes involved in heat conduction.

The simplest material to consider is the perfect electrical insulator. Many materials of both technical and scientific interest can be regarded as approximating to this. To understand the transport of heat in such a material one considers the form in which the internal energy exists. This is almost exclusively in the lattice vibrations, as the thermal motion of the atoms or ions is usually called. If a model of the solid is used where the atoms are coupled to their neighbours by forces, which, although of a quantum-mechanical nature, can be treated classically, the resultant expressions for internal energy and specific heat are in good agreement with experiment at both low, intermediate, and high temperatures. Even the Debye model, in which the lattice vibrations are treated as sound waves, gives quite an adequate picture for many purposes.

One of the most important features of models of this kind is that the vibrations are analysed into normal modes obeying harmonic oscillator equations. These harmonic oscillators are found to possess energy only in discrete integer units of $h\nu = \hbar\omega$, where ν is the oscillator frequency, $\omega (= 2\pi\nu)$ is the angular frequency, h is Planck's constant, and $\hbar = h/2\pi$. To be precise, the energy of the oscillator must be of the form

$$\mathcal{E}_n = (n + \frac{1}{2})\hbar\omega,$$

where n is an integer, and the half gives the inaccessible, but detectable, 'zero point' energy. These quanta $\hbar\omega$ are called 'phonons' in the solid by analogy with the photons of electromagnetic radiation. It is this quantisation which causes the rapid decrease in specific heat at low temperatures. From many points of view these phonons can be regarded as particles and the solid as a gas of such particles. Then heat conduction appears as a diffusion of phonons from a hotter region where they are more numerous to a colder region where they are less so. The alternative classical picture requires consideration of the varying amplitudes of lattice waves in hotter and colder regions and is considerably less vivid.

It may be shown that in an infinite perfect single crystal where the lattice vibrations are strictly harmonic there is no resistance to the flow of phonons. Departure from strict harmonicity gives rise to collisions between phonons and a thermal resistivity, $1/\lambda$, proportional to absolute temperature. This is characteristic of the high-temperature behaviour of insulators.

Phonon scattering due to the presence of impurity atoms and other point defects of the crystal lattice becomes effective at fairly low temperatures. Finally, at very low temperatures the main mechanism of phonon scattering is collision with the surface of the crystal or with grain boundaries inside a polycrystalline insulator. This gives rise to a decrease of thermal conductivity as T^3 at low temperatures. It can be seen that with $\lambda \propto T^{-1}$ at high temperatures, and $\lambda \propto T^3$ at low temperatures, there is a maximum value of λ at some intermediate temperature. This kind of behaviour characterises insulators with fairly good crystal perfection, though not ceramics or glasses.

From the point of view of analysis of the experimental data the easiest materials to understand are the pure metals. It was discovered as early as 1853 that the ratio of thermal to electrical conductivity was very similar for a large number of metals, and it was later shown that this 'Wiedemann-Franz ratio' was proportional to absolute temperature as long as the temperature was not too low. This clearly indicated that the mechanism of heat transport was the motion of the free electrons in the metal. However, this conclusion left two questions unanswered. The first was why this large number of free electrons did not contribute to the specific heat. This problem was solved by the application of quantum mechanics to the statistics of electrons. The second was what had happened to the phonon (lattice vibrational) thermal conductivity, which in many insulators is nearly as large as the thermal conductivity characteristic of pure metals. The answer to this was to be found in the scattering of phonons by electrons, an answer confirmed by the detection of a lattice contribution to the thermal conductivity in some alloys where the electrical conductivity was low, and most unambiguously by experiments on superconductors where, owing to the effective removal of the electrons into a state in which both interaction with phonons and heat transport were impossible, a large lattice thermal conductivity appears.

For most materials it is unnecessary to consider heat conduction mechanisms other than those due to electrons and phonons. As an example where one has to go beyond this, there are certain semiconductors where electrical conduction is due to electrons and positive 'holes' in nearly equal numbers, and here the energy of creating the electron-hole pair contributes to the heat transport.

1.5 General considerations in the measurement of thermal conductivity
The methods of measuring thermal conductivity can be divided into two categories, static and dynamic, depending on whether the temperature distribution within the sample is time dependent. Static measurements involve the use of equation (1.1) and it is necessary to determine the heat current density and the temperature gradient along the normal to the isothermal surface. In contrast to the steady state measurements, dynamic methods involve the complete differential heat flow equation (1.4). In general these methods determine the diffusivity and require measurement of the time for a thermal disturbance to propagate a known distance. The specific heat and density must be known in order to obtain the thermal conductivity, although in some dynamic methods the specific heat can be determined as well as the diffusivity.

Both steady state and dynamic methods require the solution of the appropriate equation for the particular geometry of the sample, heat source, and sink. The simple solutions involve isothermals which are either plane, cylindrical, or spherical surfaces. It is usually an experimental problem to maintain the isothermals of the shape required for a particular mathematical solution, because of heat transfer from the sample to the surrounding medium.

The stationary state condition assists in the achievement of a high degree of precision of measurement, although the total time involved in achieving equilibrium can be a very lengthy process if the conductivity is low. The long time constant also makes steady state methods undesirable at very high temperatures. Dynamic methods, in general, do not give as high a precision as static ones although modern instrumentation is improving enormously the precision attainable with this type of method. There has been a tremendous upsurge of interest in various dynamic techniques in the past few years with the desire to obtain data rapidly, particularly at high temperatures.

The choice of method of measurement depends upon the order of magnitude of the thermal conductivity to be evaluated, on the temperature range, and on the sample size. The latter may depend on the uniformity or macroscopic nature of the material; it may also be restricted by limitations of a manufacturing process.

The thermal conductivity of solids ranges at most over some five orders of magnitude, varying at room temperature from about $4 \text{ W cm}^{-1} \text{ K}^{-1}$ for copper or silver to $10^{-4} \text{ W cm}^{-1} \text{ K}^{-1}$ for microporous materials such as

plastic foams. For single-phase solids the spread is only over some three orders—the materials of very low conductivity are those of short range order, such as the polymers and glasses, and multiphase solids with various degrees of porosity. It is not even possible to make the generalisation that metals are better conductors of heat than nonmetals. At room temperature diamond is the best known conductor and, depending upon the quality of the gem, can have a conductivity five times greater than that of copper. Conduction in pyrolytic graphite parallel to the layer planes is of the same order of magnitude as in diamond and is higher than that of copper up to 1200 K. The conduction perpendicular to the layer planes, however, is lower by a factor of about 200.

Although the thermal conductivity of both pure metals and nonmetallic crystals increases with decreasing temperature, close to 0 K many comparatively common electrical insulators conduct heat better than, or certainly as well as, metals. At high temperatures there is a tendency for metals to conduct better than nonmetals; however the range of values steadily diminishes and at 2000 K extends only over two orders of magnitude.

As a result of the comparatively small range of thermal conductivities there is no thermal insulator in the sense of an electrical insulator. Consequently the problem common to all methods of measurement is the attainment of the conditions of heat flow required by the mathematical solutions; moreover the degree of difficulty tends to increase with increasing temperature. As a note of caution it should be remembered that, if these conditions are not met experimentally, then the data acquired are meaningless.

A glance at the wealth of thermal conductivity data published by the Thermophysical Properties Research Centre (TPRC) at Purdue University (Touloukian, 1970) shows a disparity in data probably greater than that of any other physical property. The disagreement is more than a few per cent, may be as high as an order of magnitude, and is in general far larger than the claimed precision of the data. Some differences can be expected as no two samples can be completely identical. However, as it is shown in Chapter 6, for homogeneous materials these differences should be small (except at very low temperatures) and certainly smaller than the literature suggests. Much of the diversity is due to a lack of accuracy in the data, resulting from failure to meet experimentally the required conditions of heat flow, and in this respect TPRC has critically appraised much of the data and published recommended curves. However, this is an age of new materials and, since prediction of thermal conductivity is extremely difficult, it is a property which must be investigated experimentally. In order to make new data more reliable than those of the past, apparatus for the measurement of thermal conductivity or diffusivity should be thoroughly checked for systematic errors. Although these can be difficult

to locate, particularly without experience, they can sometimes be found by repeating measurements under different experimental conditions, changing for example sample size or heat flux. The apparatus should finally be checked by measuring one or more materials of known thermal conductivity. There is no single reference material, but the standard or standards chosen to 'check' a particular apparatus should cover the full range of conductivities for which the apparatus is to be used. High-purity copper, Armco iron, various nickel alloys, and particular glasses are commonly used. For work of the highest precision a bank of reference standards is being established at the National Bureau of Standards in Washington from whom details of stock material can be obtained. Over the past few years an international cooperative measuring programme has examined, amongst other thermal properties, the thermal conductivity and diffusivity of a number of metals and nonmetals above room temperature. The report by Fitzer (1973) serves as a useful guide to the choice of reference materials, some of which are readily available.

When reporting thermal conductivity data as much information as possible should be given in order to characterise the material. This should include the source of the material, its chemical analysis, fabrication treatment, density, grain size, crystal structure, and direction of heat flow, together with details of shape, size, and orientation of any pores or additional phases in heterogeneous materials. For electrical conductors the electrical conductivity, Hall coefficient, and thermoelectric power should be specified as functions of temperature, as these are extremely useful aids to material classification.

In the following two chapters the principles involved in various steady state and dynamic methods of measurement are discussed critically without experimental detail.

1.6 A note on units

The situation as regards the units in which thermal conductivity is measured has for some time been very confused. Until recently we have had one system usually employed by engineers in English-speaking countries and two systems employed by scientists and Continental engineers. A further system based on SI Units has now appeared and will have legal force in Britain in the near future.

The first system referred to has as its basis the British thermal unit (Btu), the hour, the foot, and the degree Fahrenheit. Thus the units of thermal conductivity in this system are

$$\text{Btu h}^{-1} \text{ft}^{-1} \text{ } ^\circ\text{F}^{-1}.$$

The two systems used by scientists differ in that one uses calories and the other joules (or ergs). In the first of these we have as units of thermal conductivity

$$\text{cal s}^{-1} \text{cm}^{-1} \text{K}^{-1},$$

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20
1

whilst in the second we have

$$\text{W cm}^{-1} \text{K}^{-1},$$

where K stands for the kelvin, defined as the fraction $1/273.16$ of the thermodynamic temperature of the triple point of water [this symbol is used both for thermodynamic temperature (in place of $^{\circ}\text{K}$) and for temperature interval (in place of deg, $^{\circ}\text{C}$, $^{\circ}\text{K}$)]. The SI system is based on the second system, but insists on metres rather than centimetres, so the units are

$$\text{W m}^{-1} \text{K}^{-1}.$$

There seems to us no excuse for persisting with the $\text{Btu h}^{-1} \text{ft}^{-1} ^{\circ}\text{F}^{-1}$ system or the calorie-based metric system. At present inconvenience is caused by the existence of great quantities of data expressed in units of these systems, but to continue using them will only increase these difficulties for the future. The two remaining systems only differ by a factor of one hundred and can easily be used in harness. Except in building applications the metre seems rather a large unit to employ. Furthermore most current scientific work seems to use the $\text{W cm}^{-1} \text{K}^{-1}$ system and for these two reasons we shall use these units. Similarly we shall generally use $\text{cm}^2 \text{s}^{-1}$ for the units of diffusivity. To assist in the use of the literature a table for converting the systems of units one to another is given in the Appendix.

References

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Static methods of measuring thermal conductivity

2.1 Introduction

In static methods the thermal conductivity is obtained from measurements of a temperature gradient together with the heat flux into or out of the sample in accordance with equation (1.1).

In its simplest form the sample is a cylinder in which the heat flow is parallel to the axis and the isotherms are planes perpendicular to the axis. This is the basis of the so-called linear or axial flow method. Owing to the inevitability of heat losses it is difficult to ensure that the temperature gradient remains normal to the cross-sectional area. Moreover the problems of maintaining uniform isotherms are enhanced as the temperature of measurement is increased.

As an alternative, a sample which surrounds a heat source is used. This could be a hollow sphere with a central spherical heater or a long cylinder with the heater along the axis. In these cases the heat flow is radial and the isotherms are either spheres or infinite cylinders. This is the basis of the radial flow method.

2.2 Linear flow method

2.2.1 General principle

If all the heat supplied by the electric heater at the rate Φ is conducted along a rod of uniform cross-sectional area A with distance L between thermometers, as shown in figure 2.1, then at any point

$$\lambda = -\frac{\Phi}{A} \frac{dL}{dT}, \quad (2.1)$$

and the mean conductivity λ between the temperatures T_1 and T_2 is

$$\lambda = -\frac{\Phi \Delta L}{A \Delta T} = -\frac{\Phi L}{A \Delta T} = \frac{\Phi L}{A(T_1 - T_2)}. \quad (2.2)$$

This assumes that the heat losses from the periphery of the sample and along the thermometers are negligible. In order to ensure that the heat flow is linear between the thermometers, they should not be closer to the heater or the heat sink than a length equal to the sample diameter.

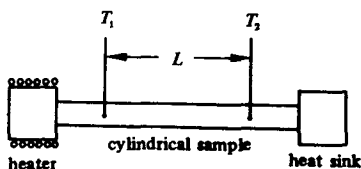


Figure 2.1. Schematic diagram for measurement of thermal conductivity under steady-state linear heat flow.

In general, measurement of the heat flow rate Φ and of the cross-sectional area A presents no problem. However, it is necessary to pay great attention to the measurement of the temperature difference ($T_1 - T_2$) along the length L . Since thermal conductivity varies with temperature, quite markedly in many cases, the temperature difference should be small so that a meaningful average temperature can be assigned to the measurement. The thermometers, which if possible should fit snugly to a reasonable depth in holes in the sample, should be as small in cross-section as practicable, since ideally the temperature at a point is required and the distance between the two points must be measured precisely. Since the accuracy is dependent upon the measurement of a difference in temperature of only a few degrees, the precision of absolute temperature measurement must be high. Alternatively, if direct measurement of the temperature difference can be made, the absolute value of either T_1 or T_2 , from which the average temperature can be assigned, can be determined with less precision. For this reason thermocouples are ideal thermometers, since the temperature difference can be measured by connecting the two thermocouples back to back. It is of course essential to maintain the cold junctions of the thermocouples at the same temperature, preferably by immersing the junctions in a suitable constant-temperature environment of high thermal mass, so that any small fluctuations in temperature have a long time constant compared with the time necessary to make the measurements. By using suitable switches, free from spurious thermoelectric effects, the voltage output from each thermocouple can be measured directly as well as the differential e.m.f. However, at low temperatures the sensitivity of thermocouples becomes comparable to, or less than that of, resistance thermometers, so that it becomes necessary to make precise measurements of each absolute temperature. It must also be remembered that heat flow from, or to, the specimen will be conducted by the thermometer leads, which should be kept as fine as possible.

The choice of specimen geometry is controlled mainly by the conductivity value to be measured, by the sensitivity of the thermometers, and by practicable values of Φ . The ratio of length to area L/A must be large enough to ensure that ΔT is sufficiently large to measure without needing an enormously large heat flux. Lateral heat losses are proportional to the surface area, so that to minimise them a short sample with a large cross-section is required. Measurement of the temperature gradient then becomes difficult since the presence of the thermometers significantly alters the heat flow pattern. This can be overcome by attaching each end of the sample to a good conducting block in which the temperature is measured; the measured temperature gradient is then likely to contain spurious gradients across the contact between the sample and block, the magnitude of which will be more significant the greater the thermal conductivity being measured. From this point of view the arrangement